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May 31, 1984

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The objective of this research was to define the chemical factors that affect onset of superconductivity in ternary compounds: to determine how small changes in stoichiometry and microstructure influence critical temperature, how the number and placing of magnetic ions act to quench superconductivity, and how the crystal structure can be modified to enhance superconductivity. The approach was to synthesize, from ultrapure starting elements, ternary borides, silicides, sulfides and selenides of the second and third row transition elements, to characterize the new compounds for x-ray structure, electrical and magnetic behavior, and then compare them with doped materials. Four kinds of compounds were investigated: rare earth osmium disilicides, rare earth osmium-iridium borides, layered structure transition metal dichalcogenides, and Chevrel type molybdenum ternaries. Both the rare earth osmium-iridium borides and rare earth osmium disilicides were synthesized by arc melting.					
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The crystal structures were refined and magnetic susceptibility studies revealed conventional Hunds's rule behavior in the disilicides while the (Pr, Nd) (Os, Ir) $4B_4$ compounds are characterized by Van Vleck paramagnetism of closely spaced multiplets. Only $LaOs_2Si_2$ and $LuOs_2Si_2$ compounds are superconducting with T_c 's in the 2-4K range. ²In the layered compounds, lithium intercalated ZrS_2 , $ZrSe_2$, NbS_2 , and $NbSe_2$ were studied. Tx behavior of $2H-LiNbSe_2$ is determined principally by the ²variation in the electronic density of states at the Fermi level, whereas the T_c behavior of $2H-LiNbS_2$ is further modified by a charge density wave, a form of incipient metal-metal² bonding, and by interlayer lithium ordering. The stability of different polytypes dominates the superconducting behavior of the zirconium systems. The Chevrel phases were probed to study the effect of electron concentration, magnetic ions, and disorder upon the superconductivity in these materials. Additionally a correlation was found between a structural instability in the $M^{+2}Mo_6S_8$ compounds and superconductivity.

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ABSTRACT

The objective of this research was to define the chemical factors that affect onset of superconductivity in ternary compounds: to determine how small changes in stoichiometry and microstructure influence critical temperature, how the number and placing of magnetic ions act to quench superconductivity, and how the crystal structure can be modified to enhance superconductivity. The approach was to synthesize, from ultrapure starting elements, ternary borides, silicides, sulfides and selenides of the second and third row transition elements, to characterize the new compounds for x-ray structure, electric and magnetic behavior, and then compare them with doped materials. Four kinds of compounds were investigated: rare earth diosmium disilicides, rare earth osmium-iridium borides, layered structure transition metal dichalcogenides, and Chevrel type molybdenum ternaries. Both the rare earth osmium-iridium borides and rare earth diosmium disilicides were synthesized by arc melting. The crystal structures were refined and magnetic susceptibility studies revealed conventional Hund's rule behavior in the disilicides while the $(\text{Pr}, \text{Nd})(\text{Os}, \text{Ir})_4\text{B}_4$ compounds are characterized by Van Vleck paramagnetism of closely spaced multiplets. Only LaOs_2Si_2 and LuOs_2Si_2 compounds are superconducting with T_c 's in the 2-4K range. In the layered compounds, lithium intercalated ZrS_2 , ZrSe_2 , NbS_2 , and NbSe_2 were studied. T_c behavior of 2H-LiNbSe_2 is determined principally by the variation in the electronic density of states at the Fermi level, whereas the T_c behavior of $2\text{H-Li}_x\text{NbS}_2$ is further modified by a charge density wave, a form of incipient metal-metal bonding, and by interlayer lithium ordering. The stability of different polytypes dominates the superconducting behavior of the zirconium systems. The Chevrel phases were probed to study the effect of electron concentration, magnetic ions, and disorder upon the superconductivity in these materials. Additionally, a correlation was found between a structural instability in the $\text{M}^{+2}\text{Mo}_6\text{S}_8$ compounds and superconductivity.

SUMMARY

The principal accomplishments during this grant period were:

- (1) synthesis and characterization of a new rare earth osmium-silicide series;
- (2) synthesis and characterization of a new series of rare earth osmium-iridium borides;
- (3) mapping out the superconductivity behavior in the pseudoternary system (Y, Lu, Th)Rh₄B₄;
- (4) Tc and crystallographic study of lithium intercalated ZrS₂, ZrSe₂, and NbS₂, and NbSe₂;
- (5) magnetic study as a function of composition of the high-temperature superconductor Li_xTi_{2-x}O₄;
- (6) synthesis of mixed lithium-magnesium titanium spinels;
- (7) magnetic and superconducting study over the whole pseudobinary system YbMo₆S₈-YbMo₆Se₈. where we showed that contrary to a report in the literature, the selenide end member of the series is not a superconductor under the conditions studied;
- (8) density of state studies in rare earth molybdenum chalcogenides as deduced from chemical substitution effects on superconductivity;
- (9) study of chalcogen ordering on special position sites in ternary molybdenum chalcogenides;
- (10) magnetic, magnetic resonance, and superconductivity studies in the pseudobinary systems EuMo₆S₈-EuMo₆Se₈ and LaMo₆Se₈-EuMo₆Se₈;
- (11) magnetic and superconductivity study on the mixed system SmMo₆(S_{1-x}Se_x)₈;
- (12) magnetic study of phase instabilities of the AgMo₆(S_{1-x}Se_x)₈ system;
- (13) study of phase instabilities and their relationship to superconductivity in the M⁺²Mo₆S₈ system.



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The details of these findings are as follows:

(1) (Kurt Hiebl and Peter Rogl) A new series of rare earth diosmium disilicides has been synthesized by arc melting. The structure type is that of ThCr_2Si_2 . The crystallographic parameters, particularly the unit-cell volume and the c axis show a perfectly regular linearity with trivalent ion radius, except for a pronounced anomaly at cerium. Magnetic susceptibility measurements, over the range 4-1000K show conventional Hund rule behavior for all the series except samarium. The lanthanum and lutetium members are superconducting with T_c 's in the 2-4K range.

(2) (Kurt Hiebl and Peter Rogl) The crystal structure of NdOs_4B_4 was refined as the NdCo_4B_4 type structure. Complete solid solution was found for mixed crystals LaOs_4B_4 - LaIr_4B_4 . Magnetic susceptibility studies over the range 1.8-1100K showed that $(\text{Pr},\text{Nd})(\text{Os},\text{Ir})_4\text{B}_4$ compounds are characterized by Van Vleck paramagnetism of closely spaced multiplets. For the $\text{La}(\text{Os},\text{Ir})_4\text{B}_4$ series, a small (constant) paramagnetic moment of $0.1\mu_B$ was derived, possibly attributable to the lanthanum. In the case of PrIr_4B_4 , ferromagnetic ordering was observed at very low temperature. No superconductivity was found down to 1.5K. The new ternary metal borides, EuOs_4B_4 and EuIr_4B_4 were synthesized, found to have the NdCo_4B_4 type structure, and magnetism corresponding to free Eu^{+2} ions. Complete solid solution was found in the series CeOs_4B_4 - CeIr_4B_4 with magnetic behavior changing from that of a pure Ce^{+4} state for the osmium compound to Ce^{+3} for the iridium.

(3) (Kurt Hiebl and Peter Rogl) Superconductivity was studied in the pseudoternary system YRh_4B_4 - LuRh_4B_4 - ThRh_4B_4 as nonmagnetic analogs of RERh_4B_4 . Isocritical temperatures as well as isochores were established. A minimal critical temperature was found in the pseudobinary system $\text{Y}_x\text{Lu}_{1-x}\text{Rh}_4\text{B}_4$ at 10.1K and $x = 0.5$. The pair-breaking influence of magnetic RE ions was worked out in good agreement with the Abrikosov-Gorkov theory for

isotropic elastic exchange scattering of conduction electrons by randomly distributed and noninteracting localized magnetic moments.

(4) (Craig McEwen) Li_xNbS_2 and Li_xNbSe_2 , where $0 < x < 1$, were prepared by high temperature synthesis to examine the effect of lithium intercalation on the superconducting critical temperature of the host materials. Li_xZrS_2 and Li_xZrSe_2 , where $0 < x < 1$ were similarly prepared to determine if superconductivity could be induced in the non-superconducting host materials: at $x = 1$, these materials should be isoelectronic with NbS_2 ($T_c = 6.5\text{K}$) and NbSe_2 ($T_c = 7.4\text{K}$), respectively.

It was found that the behavior of $2\text{H-Li}_x\text{NbSe}_2$ is determined principally by the variation in the electronic density of states at the Fermi level, whereas the T_c behavior of $2\text{H-Li}_x\text{NbS}_2$ is further modified by a charge density wave, a form of incipient metal-metal bonding, in the range $0.0 < x < 0.33$ and by inter-layer lithium ordering (staging) around $x = 0.083$ ($1/12$), $x = 0.143$ ($1/7$), and $x = 0.33$ ($1/3$). Such ordering was found in $2\text{H-Li}_x\text{NbSe}_2$ where it has less of an effect on T_c . $2\text{H-Li}_x\text{NbS}_2$ coexists with $3\text{R-Li}_x\text{NbS}_2$ in the range $0.01 < x < 0.15$; the 3R phase was found to superconduct as well. The existence of amorphous superconducting 3R-NbS_2 was inferred. Additionally, a CDW in the lithium-intercalated 3R materials is proposed.

Various phases were identified in the Li_xZrS_2 and Li_xZrSe_2 series: with increasing lithium concentration, Li_xZrSe_2 proceeds from a 1T to a 3R phase. Magnetic susceptibility measurements suggest that localization of electrons in $\text{Zr}^{3+}\text{-Zr}^{3+}$ pairs occurs in the 1T and 3R' phases of Li_xZrS_2 . ESR measurements confirm the existence of localized electrons. Li_xZrS_2 and Li_xZrSe_2 were also prepared by reaction with n-butyllithium under ambient conditions: the resulting metallic compounds had a different structure than those prepared at high temperature. Apparently electrons in the materials synthesized at high temperatures become localized in metal-metal bonds, explaining why superconductivity is not observed in these materials.

(5) (Martin R. Harrison) The magnetic susceptibility, ESR and superconductivity have been studied over the range 4.2– 300K for the spinel system $\text{Li}(\text{Li}_x\text{Ti}_{2-x})\text{O}_4$ as a function of composition. When $x=0$, the material is Pauli paramagnetic, metallic and superconducting ($T_c=11\text{K}$); when $x=1/3$, diamagnetic, and insulating. The system is unstable to oxidation of Li^+ and Ti^{3+} ions which coexist on octahedral sites. This instability, which is most pronounced at $x=1/11$, is overcome if the lithium ions are lost on firing. However, the material is then unstable to disproportionation into non-metallic and metallic, superconducting regions. The latter form percolating pathways and the material exhibits metallic properties over most of the homogeneity range ($0 < x < 1/3$). A transition does not appear to occur until x is close to $1/3$. The composition with $x=1/3$ can be reduced in hydrogen, but these reduced materials exhibit nonmetallic properties; the electrons are localized by the disorder created by the reduction. Electrons are trapped at oxygen vacancies and interstitial protons in both the unreduced and reduced materials.

(6) (Martin Harrison and Pat Lambert) The spinel MgTi_2O_4 has been successfully synthesized from MgO and Ti_2O_3 by rf heating for 4–5 hours at 1100°C . The mixed spinel $\text{Li}_{1-x}\text{Mg}_x\text{Ti}_2\text{O}_4$ has also been made, but there is considerable loss of lithium. Two ESR signals are obtained with a curious peaking of line width and g-factor shift at about 120 K. Attempts are still under way to lessen the loss of lithium during preparation.

(7) (David Johnson and Jean-Marie Tarascon) The pseudobinary systems YbMo_6S_8 – YbMo_6Se_8 were investigated for magnetic and superconducting behavior to find out why, of the rare earth molybdenum chalcogenides, ytterbium is anomalously high in the sulfide series and anomalously low in the selenide series. The superconducting critical temperatures showed a monotonic decrease from 8.65 K for the fully sulfided member to less than 1.6 K for the all selenium sample; but Faraday susceptibility studies showed more magnetic ion ($3.3\% \text{Yb}^{3+}$)

in the sulfide than in the selenide ($1.3\% \text{ Yb}^{3+}$). Superconductivity of the selenide, as erroneously reported in the literature over the range 4.7–5.8 K, could be reproduced with nonstoichiometric material $\text{Yb}_{1+x}\text{Mo}_6\text{Se}_8$ ($T_c = 5.6\text{--}5.8$) but x-ray studies showed presence of a second phase corresponding to Mo_6Se_8 which normally has $T_c = 6 \text{ K}$.

(8) (Jean-Marie Tarascon and David C. Johnson) The pseudobinary systems $\text{YbMo}_6\text{S}_8\text{--LaMo}_6\text{S}_8$ and $\text{YbMo}_6\text{Se}_8\text{--LaMo}_6\text{Se}_8$ have been investigated to trace out the effect of replacing a two-electron donor, ytterbium, by a three electron donor, lanthanum, on the crystal structure parameters and on the superconducting critical temperatures. The effect of selenium for sulfur replacement in the system $\text{LaMo}_6\text{S}_8\text{--LaMo}_6\text{Se}_8$ has been similarly explored. The results are used to derive quantitative information about the effect of unit cell volume and of electron donation on the shape of the density of states curve. It is evident that a rigid band model does not hold. Selenium for sulfur replacement, as expected, narrows the d -orbital derived conduction band. Apparently, LaMo_6Se_8 lies at the upper van Hove singularity, whereas YbMo_6Se_8 falls in the minimum between the upper and lower van Hove peaks.

(9) (David C. Johnson and Jean Marie Tarascon) The effect on crystallographic parameters of selenium for sulfur replacement has been studied in several series of ternary molybdenum chalcogenides of the Chevrel-phase type. In all the systems examined— $\text{MMo}_6(\text{S}_{1-x}\text{Se}_x)_8$ with $M = \text{La, Ce, Sm, Eu, Yb, Pb, Ag}$ and $0 < x < 1$ — the hexagonal c/a ratio shows a minimum when plotted against the percent sulfur replaced. The minimum is shallowest for the case of Ag and deepest for the case of La and Ce. The apparent cause of the minimum is the strong preference by the selenium for occupancy of the general position chalcogen site rather than the special position site on the $\bar{3}$ axis. The preferred site ordering is greater for M^{3+} than for M^{2+} or M^+ . Delocalization of M off the $\bar{3}$ axis decreases the ordering, as it tends to increase the bonding in the a direction.

(10) (Jean Marie Tarascon, Martin R. Harrison, and David C. Johnson)

Magnetic susceptibility measurements have been carried out by the Faraday method over the range 4.2 - 300 K on a series of phases of composition $\text{Eu}_{1.2}\text{Mo}_6(\text{S}_{1-x}\text{Se}_x)_8$ where $0 < x < 1$. No magnetic ordering and no superconductivity was observed; the europium is essentially divalent over the whole range of composition. Superconducting critical temperatures, measured by an ac mutual inductance technique, show, for the series $\text{La}_{1-x}\text{Wu}_x\text{Mo}_6\text{Se}_8$, roughly the same behavior as found for $\text{La}_{1-x}\text{Yb}_x\text{Mo}_6\text{Se}_8$ and can be accounted for in terms of the theory of Abrikosov and Korkov. ESR spectra, measured from 4.2 to 300 K at X-band frequency, are quite different for $\text{Eu}_{1.2}\text{Mo}_6\text{X}_8$ and $\text{Eu}_{1.0}\text{Mo}_6\text{X}_8$. Furthermore, in some of the $\text{Eu}_{1.2}\text{Mo}_6\text{S}_{8-x}\text{Se}_x$ samples, the temperature study reveals a phase change in the ESR signal around 110 K. The signals, quite surprising for Eu^{2+} , can be interpreted by assuming a spin Hamiltonian containing a crystal field term that is large compared to the Zeeman splitting.

(11) (David C. Johnson and Jean Marie Tarascon) Magnetic susceptibility measurements have been carried out by the Faraday method over the range 4.2 - 300 K and superconducting critical temperatures measured for the solid solution $\text{SmMo}_6(\text{S}_{1-x}\text{Se}_x)_8$. The susceptibility studies indicate that the samarium is in the 3+ oxidation state. The moment obtained for the samarium varies as the symmetry of the chalcogen cube changes throughout the solid solution. This indicates that crystal field effects are important in these materials.

(12) (David C. Johnson) The silver solid solution, involving a mix of sulfur and selenium, was investigated and room temperature X-ray measurements showed that the solid solution was single phased. The c/a ratio in this series did not vary with composition. Susceptibility measurements over the temperature range 3-300 K were performed and the data suggest that a structural instability occurs in the selenium rich compositions. The anomaly, marked by a sharp decrease in the observed susceptibility, indicates a reduction in the density of states at the Fermi level. The structural instability is either a distortion in the molybdenum octahedron or a localization of the silver atom either on or off of the 3 axis.

(13) (David C. Johnson and Nathalie Chevreau) The $M^{+2}Mo_6S_8$ compounds ($M = Pb, Sn, Eu, Yb, Ba, Sr, Ca$) all were found to have a lattice instability. The temperature at which the molybdenum octahedra distorts is a function of the bonding differences between the different ternary metals and is related to the electron polarizability of the cation. The lattice distortion temperature was found to be inversely proportional to the observed superconducting critical temperature as a result of the localization of electrons from the conduction band to intracuster molybdenum-molybdenum bonds when the structure distorts. This observation was then extended to the $PbMo_6(S_{1-x}Se_x)_8$ solid solution.

(14) (Nathalie Chevreau and David C. Johnson) A new low temperature technique was devised to synthesize the previously unknown phases, $SbMo_6Se_8$ and $BiMo_6S_8$. The procedure used was to leach out the copper from the phases $Cu_{1.8}Mo_6S_8$ via a solution of iodine in acetonitrile. The resulting material, Mo_6S_8 , was then heated with the ternary element, antimony or bismuth, up to 600 °C in a sealed quartz tube. The resulting compounds were characterized by X-ray diffraction and DTA and found to be single phased. The $BiMo_6S_8$ samples were found to superconduct in the 3-5 K range.

PERSONNEL

In addition to the principal investigator, Professor M. J. Sienko, the following people were associated with this project during various parts of the grant period:

A. Postdoctoral Associates

Dr. Martin R. Harrison (4/9/81 - 4/8/83)
Dr. Nathalie Chevreau (8/19/82 - 5/10/84)
Dr. Kurt Hiebl (7/26/78 - 8/31/83)
Dr. Jean Marie Tarascon (9/15/80 - 12/23/81)
Dr. Peter Rogl (7/81 - 8/81)
Dr. David C. Johnson (10/83 - 3/84)

B. Research Assistants

David C. Johnson
Craig McEwen
Eric Bell
Dell St. Julien
Pat Lambert
David Guy

Two Ph.D. degrees were completed during this period, that of Craig McEwen on "Structure and Physical properties of Lithium Intercalated Zirconium and Niobium Dichalcogenides" and that of David C. Johnson on "Structure and Physical Properties of the Ternary Molybdenum Chalcogenides".

PUBLICATIONS

The following papers containing AFOSR acknowledgement were published, accepted for publication, or submitted for publication during the report period:

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